Designation: ~~D6144 – 17~~ D6144 – 22

Standard Test Method for
Analysis of AMS (α-Methylstyrene) by Capillary Gas Chromatography[1]

1. Scope*

1.1 This test method covers the determination of the purity of AMS (α-methylstyrene) by gas chromatography. Calibration of the gas chromatography system is done by the external standard calibration technique.

1.2 This test method has been found applicable to the measurement of impurities such as cumene, 3-methyl-2-cyclopentene-1-one, *n*-propylbenzene, *tert*-butylbenzene, *sec*-butylbenzene, *cis*-2-phenyl-2-butene, acetophenone, 1-phenyl-1-butene, 2-phenyl-2-propanol, *trans*-2-phenyl-2-butene, *m*-cymene, *p*-cymene, and phenol, which are common to the manufacturing process of AMS. The method has also been found applicable for the determination of para-tertiary-butylcatechol (TBC or PTBC) typically added as a stabilizer to AMS. The impurities in AMS can be analyzed over a range of 5 to 800 mg/kg by this method. (See ~~Table 1.) The~~ Table 2.) Based on the results in ASTM Research Report RR:D16-1022, summarized in Table 2, the limit of quantitation for these ~~these~~ impurities averages 4 mg/kg, while the limit of detection averages ~~1.2~~1.2 mg ~~mg/kg. (See~~/kg. ~~Table 1.)~~

1.3 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate* ~~safety~~ *safety, health, and* ~~health~~*environmental practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see Section* 8.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D3437 Practice for Sampling and Handling Liquid Cyclic Products
D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals
D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

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A Summary of Changes section appears at the end of this standard

TABLE ~~1~~2 Summary of Precision Data (mg/kg)

Compound	Repeatability (r)	Reproducibility (R)	Range Studied
Acetone	1.61 + 0.035*Acetone	0.47 + 1.10*Acetone	0.5 – 26
~~Cumene~~	~~–0.46 + 0.031*Cumene~~	~~7.88 + 0.19*Cumene~~	~~45 – 290~~
Cumene	–0.46 + 0.031*Cumene	7.88 + 0.19*Cumene	45 – 290
~~nPropylbenzene (NPB)~~	~~2.11 + 0.03*NPB~~	~~–7.81 + 0.37*NPB~~	~~55 – 195~~
n-Propylbenzene (NPB)	2.11 + 0.03*NPB	–7.81 + 0.37*NPB	55 – 195
Phenol	1.84	3.65 + 0.58*Phenol	1 – 40
~~tertButylbenzene (TBB)~~	~~–1.22 + 0.035*TBB~~	~~3.63 + 0.087*TBB~~	~~150 – 650~~
tert-Butylbenzene (TBB)	–1.22 + 0.035*TBB	3.63 + 0.087*TBB	150 – 650
~~secButylbenzene (SBB)~~	~~4.23 + 0.019*SBB~~	~~21.60 + 0.25*SBB~~	~~200 – 765~~
sec-Butylbenzene (SBB)	4.23 + 0.019*SBB	21.60 + 0.25*SBB	200 – 765
~~mCymene~~	~~0.31 + 0.035*mCymene~~	~~2.34 + 0.35*mCymene~~	~~2 – 50~~
m-Cymene	0.31 + 0.035*mCymene	2.34 + 0.35*mCymene	2 – 50
~~oCymene~~	~~1.63~~	~~8.00~~	~~29 – 31~~
o-Cymene	1.63	8.00	29 – 31
~~pCymene~~	~~5.12~~	~~15.79~~	~~10 – 18~~
p-Cymene	5.12	15.79	10 – 18
cis-2-Phenyl-2-Butene (CPB)	0.17 + 0.030*CPB	5.39 + 0.11*CPB	50 – 225
~~trans-2-Phenyl-2-Butene (TPB)~~	~~1.57~~	~~0.54 + 0.20*TPB~~	~~19 – 70~~
trans-2-Phenyl-2-Butene (TPB)	1.57	0.54 + 0.20*TPB	19 – 70
1-Phenyl-1-Butene (PB)	4.00 + 0.018*PB	0.17 + 0.19*PB	0.2 – 735
Acetophenone (AP)	–1.09 + 0.15*AP	1.17 + 0.63*AP	15 – 115
para-tert-Butylcatechol (PTBC)	2.21	17.82	10 – 19
2-Methylbenzofuran (MBF)	0.33 + 0.76*MBF	0.75 + 0.60*MBF	1 – 2
2-Phenylpropion aldehyde (PPA)	0.59 + 0.11*PPA	0.29 + 0.23*PPA	1.5 – 15
α-Methylstyrene Oxide (AMSO)	4.61	6.51 + 0.23*AMSO	13 – 32
DimethylBenzyl Alcohol (DMBA)	0.38	0.55 + 2.03*DMBA	0.1 – 1

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E355 Practice for Gas Chromatography Terms and Relationships
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs
2.2 *Other Document:*
OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200[3]

3. Terminology

3.1 See Terminology D4790 for definition of terms used in this test method.

4. Summary of Test Method

4.1 AMS (α-methylstyrene) is analyzed by a gas chromatograph (GC) equipped with a flame ionization detector (FID). A precisely repeatable volume of the sample to be analyzed is injected onto the gas chromatograph. The peak areas of the impurities are measured and converted to concentrations via an external standard methodology. Purity by GC (the AMS content) is calculated by subtracting the sum of the impurities from 100.00. ~~Results~~ Purity results are reported in ~~weight~~mass percent.

5. Significance and Use

5.1 This test method is suitable for setting specifications on the materials referenced in 1.2 and for use as an internal quality control tool where AMS is produced or is used in a manufacturing process. It may also be used in development or research work involving AMS.

5.2 This test method is useful in determining the purity of AMS with normal impurities present. If extremely high boiling or unusual impurities are present in the AMS, this test method would not necessarily detect them and the purity calculation would be erroneous.

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[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

6. Apparatus

6.1 *Gas Chromatograph*—Any instrument having a flame ionization detector that can be operated at the conditions given in Table ~~2~~1. The system should have sufficient sensitivity to obtain a minimum peak height response for ~~10~~10 mg ~~mg/kg~~/kg acetophenone of twice the height of the signal background noise.

6.2 *Columns*—The choice of column is based on resolution requirements. Any column may be used that is capable of resolving all significant impurities from AMS. The column described in Table ~~2~~1 has been used successfully and shall be used as a referee in cases of dispute.

6.3 *Recorder*—Chromatographic data systems are preferred but electronic integration may be used if the user can demonstrate that the results are consistent with the precision statement. Recorders are not considered adequate for meeting the precision requirements of this standard.

6.4 *Injector*—The specimen must be precisely and repeatably injected into the gas chromatograph. An automatic sample injection device is highly recommended. Manual injection can be employed if the precision stated in ~~Table 1~~Table 2 can be reliably and consistently satisfied.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

TABLE ~~2~~1 Recommended Operating Conditions

Detector	flame ionization
Injection Port	capillary splitter
Column A:	
Tubing	fused silica
Stationary phase	crosslinked methylsilicone
Film thickness, ÷µm	1.0
Length, m	60
Diameter, mm	0.32
Temperatures:	
Injector, °C	250
Detector, °C	300
~~Oven, °C~~	~~85 hold for 13 min~~
	~~Ramp 1 = 6°C/min to 125°C, hold for 2 min~~
	~~Ramp 2 = 30°C/min to 250°C, hold for 7.5 min~~
Oven, °C	85 hold for 13 min
	Ramp 1 = 6 °C /min to 125 °C, hold for 2 min
	Ramp 2 = 30 °C /min to 250 °C, hold for 7.5 min
Carrier gas	helium
~~Flow rate, mls/min~~	~~3~~
Flow rate, mL/min	3
Split ratio	60:1
~~Sample size, ÷µl~~	~~1.0~~
Sample size, ÷µL	1.0

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[4] *Reagent Chemicals, American Chemical Society Specifications,*ACS *Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, DC. For ~~Suggestions~~suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.2 *Carrier Gas, Makeup, and Detector Gases*—Helium, hydrogen, nitrogen, or other carrier, makeup and detector gases 99.999 % minimum purity. Oxygen in carrier gas less than ~~1 ppm,~~ 1 ppm, less than ~~0.5 ppm~~ 0.5 ppm is preferred. Purify carrier, makeup, and detector gases to remove oxygen, water, and hydrocarbons. **Warning**—Helium carrier, makeup, and detector gas was used to develop this standard. Use of other gases requires different conditions. The user must conduct the necessary evaluation to determine that equivalent results are obtained.

7.3 *Compressed Air*—Purify air to remove water and hydrocarbons. Air for a FID should contain less than ~~0.1 ppm THC.~~ 0.1 ppm THC (total hydrocarbon content).

7.4 *Equipment Setup Check Sample:*

7.4.1 For GC standards, a setup check sample should be included to:

7.4.1.1 Determine retention times for the components measured in GC standards,

7.4.1.2 Verify there is adequate resolution to measure the components of interest in GC standards, and

7.4.1.3 Determine that the equipment has the sensitivity specified in the scope of the standard.

7.4.2 For GC standards and standards that determine trace levels, the equipment setup check sample should contain a component with a concentration that is approximately two times the LOD stated in the scope of the standard. When the equipment setup check sample is analyzed, an acceptable result for the trace component is ±50 % of the expected concentration.

7.4.2.1 For GC standards where the primary material cannot be purified so that no impurities are detected, the following is suggested:
   (1) Add an impurity that is not present in the primary material. Determine that the impurity has the following properties:
   (a) The impurity is essentially inert and unreactive in the primary material;
   (b) The retention time is sufficiently separated from other impurities so that there will be no mistake in identification;
   (c) The impurity is completely vaporized in the injection port;
   (d) The impurity is well behaved on the column, that is, no fronting or tailing;
   (e) The response factor is known and not significantly different from the components of interest; and
   (f) A straight chain hydrocarbon will work for most materials. Undecane has been used as the internal standard to determine the purity of *p*-xylene.

7.5 *Pure Compounds for* ~~Calibartion~~ *Calibration*—The purity of all reagents should be 99.9 % or greater. If the purity is less than 99 %, the concentration and identification of impurities must be known so that the composition of the standard can be adjusted for the presence of the impurities.

8. Hazards

8.1 Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this test method.

9. Sampling and Handling

9.1 Sample the material in accordance with Practice D3437.

10. Preparation of Apparatus

10.1 Follow manufacturer's instructions for mounting and conditioning the column into the chromatograph and adjusting the instrument to the conditions described in Table ~~2~~1 allowing sufficient time for the equipment to reach equilibrium. See Practice E1510 for more information on column installation. See Practice E355 for additional information on gas chromatography practices and terminology.

11. Calibration

11.1 Prepare a synthetic mixture of high purity AMS containing impurities at concentrations representative of those expected in the samples to be analyzed in accordance with Practice D4307. The weight of each hydrocarbon impurity must be measured to the nearest 0.1 mg. Because the availability of stock AMS with a purity higher than 99.80 % is problematic, the method of standard additions may be required for impurities such as *tert*-butylbenzene and ~~*n*-proplybenzene,~~ -propylbenzene, as well as for a number of the other impurities listed in 1.2 that are commonly present. In addition, nearly all commercially available AMS is stabilized with 10 to 30 mg/kg of ~~para-tertiary-butylcatechol,~~ para-tertiary-butylcatechol (commonly abbreviated PTBC or TBC), requiring a standard addition methodology for this component as well unless AMS can be obtained safely and directly from the point of manufacture.

11.2 Inject the resulting solution from 11.1 into the gas chromatograph, collect and process the data. A typical chromatogram is illustrated in Fig. 1 based on the conditions listed in Table ~~2~~1.

11.3 Determine the response factor for each impurity in the calibration mixture as follows:

$$Rfi = Ci/Ai \tag{1}$$

where:

Rfi = response factor for impurity i,
Ci = concentration of impurity i in the calibration mixture, and
Ai = peak area of impurity i.

11.4 Initially analyze the calibration solution a minimum of three times and calculate an average Rfi. Subsequent calibrations may be a single analysis as long as the Rfis for all components of interest are within ±5 % of the initial validation Rfis. A "rolling" average as defined by most modern chromatographic software may also be used. The Rfi for *tert*-butylbenzene is used for the quantification of unknown impurities.

12. Procedure

12.1 Inject into the gas chromatograph an appropriate amount of sample sufficient to satisfy the sensitivity conditions detailed in 6.1 and start the analysis.

12.2 Obtain a chromatogram and peak integration report. Fig. 1 illustrates a typical analysis of AMS using the column and conditions outlined in Table ~~2~~1.

13. Calculations

13.1 Of the impurities identified in AMS, only the butenylbenzene isomers are not available commercially. However, pure samples of these isomers can be prepared, and testing has shown that all three isomers have the same response factor ±5 %, and that it is equivalent to that for *tert*-butylbenzene ±5 %.[5]

13.2 Calculate the concentration of each impurity as follows:

$$C_i = (Ai)\,(Rfi) \tag{2}$$

where:

C_i = concentration of component i, in mg/kg,
Ai = peak area of component i, and
Rfi = response factor for component i.

13.3 Calculate the total concentration of all impurities in ~~wt.~~mass % as follows:

$$C_t = \Sigma C_i/10000 \tag{3}$$

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1022. Contact ASTM Customer Service at service@astm.org.